Insights on the operation of Me-S batteries: a modeling perspective

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Motivation

Development, understanding & rational design of Metal-Sulfur batteries

Mg-Sulfur batteries:

+ High volumetric energy density
+ Cheap & abundant materials
− Low rate performance
− Short cycle life

➔ Transfer of knowledge & methodologies from Li-Sulfur

Cell model [1]

- Electrolyte

Mass conservation:

$$\frac{\partial \varepsilon_{\text{elyte}} c_i}{\partial t} = -\nabla N_i + \sum_m a_m^v \nu_{i,m}\, r_{i,m}$$

Charge conservation:

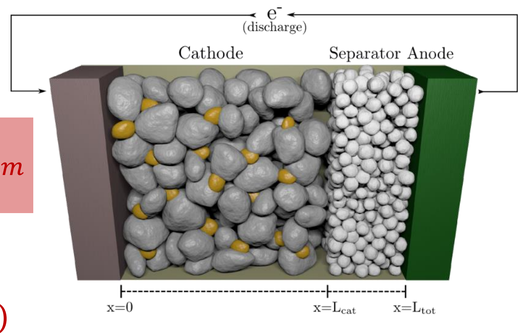
$$0 = \sum_i z_i F \left(-\nabla N_i + \sum_m a_m^v \nu_{i,m} r_{i,m} \right)$$

Species flux by Nernst-Planck equation (Diffusion + Migration):

$$N_i = -D_i \nabla c_i - z_i \frac{F}{RT} D_i c_i \nabla \phi_{\text{eylte}}$$

- Solids (charge conservation)

$$0 = -\kappa_{\text{elode}}^{eff} \nabla \phi_{\text{elode}} - \sum_{m \in \text{CTR}} a_m^v n_m F r_{i,m}$$



Reaction rate (Butler-Volmer-Type):

$$r_m = k_f^0 \frac{a_{\text{ed}}^{1-\alpha} a_{\text{prod}}^{\alpha}}{\gamma} \left(e^{-\frac{\alpha}{RT}\Delta\bar{\mu}_m} - e^{-\frac{\alpha}{RT}\Delta\bar{\mu}_m} \right)$$

$$\Delta\bar{\mu}_m = nF\left(\phi_{\text{elode}} - \phi_{\text{elyte}} - U_{\text{eq}}\right) \text{ where } U_{\text{eq}} = U_{\text{eq}}^{\ominus} + RT \ln \frac{a_{\text{prod}}}{a_{\text{ed}}}$$

Particle model [2]

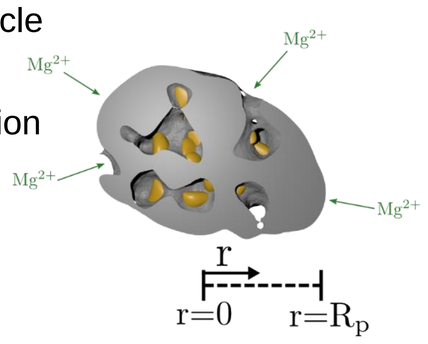
➔ The whole cell model in a spherical particle

- Coupling to cell model
  - Electrolyte: Mass & charge conservation

$$\dot{N}_i\Big|_{r=R_p} = -D_i \left(\frac{\partial c_i}{\partial r}\Big|_{r=R_p} + z_i \frac{F}{RT} D_i c_i \frac{\partial \phi_e}{\partial r}\Big|_{r=R_p} \right)$$

  - Carbon matrix: Same potential

$$i_F^{\text{mac}}|_{r=R_p} = \int \frac{4\pi r^2 i_F(r) dr}{4\pi R_p^2}$$



Nucleation & growth

- Previous work [2]: Phenomenological treatment

$$\frac{\partial \varepsilon_k}{\partial t} = \frac{\text{MW}_k}{\rho_k} \sum_m a_m^v \nu_{k,m}\, r_m$$

➔ Surface passivation: $a_m^v = a_{m,0}^v \left(\frac{\varepsilon_{\text{elyte}}}{\varepsilon_0} \right)^{1.5}$

➔ Pore clogging: $\varepsilon_{\text{elyte}} = 1 - \sum_k \varepsilon_k$

$$r_m = k_f^0 \frac{a_{\text{ed}}^{1-\alpha} a_{\text{prod}}^{\alpha}}{\gamma} \left(e^{-\frac{\alpha}{RT}\Delta\bar{\mu}_m} - e^{-\frac{\alpha}{RT}\Delta\bar{\mu}_m} \right) \text{ where } \Delta\bar{\mu}_m = RT \ln\left(\text{K}_{\text{sp}} \frac{a_{\text{prod}}}{a_{\text{ed}}} \right)$$

- Now: Classical theory of nucleation & growth

Particle size distribution $N_k(r) = f_k(r)\, dr$:

$$\frac{\partial f_k(r)}{\partial t} = \frac{\dot{N}_k^{\text{nuc}}}{dr_0} \delta_0 - \frac{\partial}{\partial r}\left(f_k \frac{dr_k}{dt} \right)$$

Nucleation... (surface energy [3])

$$\Delta G = 4\pi r_k^2 \gamma + \frac{4}{3}\pi r_k^3 \Delta G_v$$

$$\dot{N}_k^{nuc} = N_0\, Z\, D_i\, a^2 \exp\left(-\frac{\Delta G_{\text{crit}}}{k_B T} \right)$$

... and growth

$$\frac{dr}{dt} = \frac{D\, v_k^m c_i}{r_k + (D/k^0)} (1 - S_i)$$

Volume fraction:

$$\varepsilon_k = \int \frac{4}{3}\pi r^3 f_k(r_k) dr_k$$

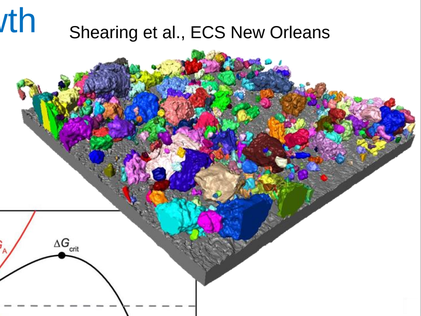
➔ $\varepsilon_{\text{elyte}} = 1 - \sum_k \varepsilon_k$

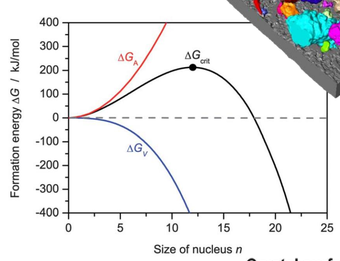
Surface area:

$$a_k^v = \int \pi r^2 f_k(r_k) dr_k$$

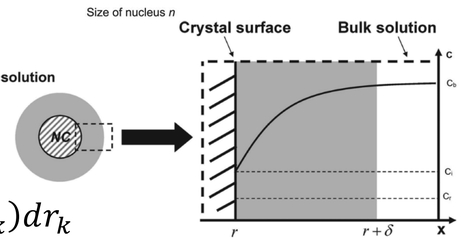
➔ $a_m^v = a_m^{v,0} - \sum_k a_k^v$

Shearing et al., ECS New Orleans





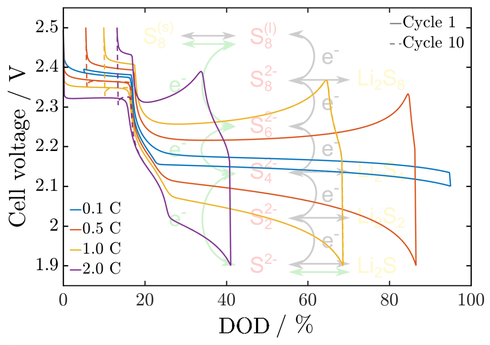
Horstmann, B. *et al.*, *Energy Environ. Sci.* **6,** 1299 (2013).



Thanh, N. T. K. et al., *Chem. Rev.* **114,** 7610–7630 (2014).

Li-S cell simulation

- Discharge & charge simulations



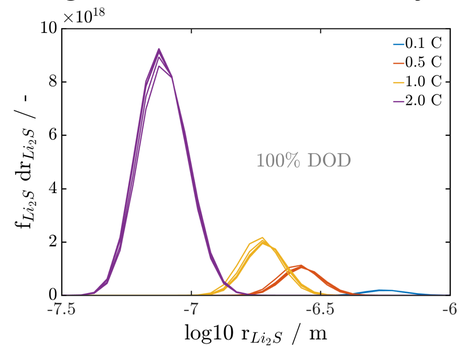
- Initially homogeneous S_8 particle size distribution & no Li_2S
  ➔ Dissolution of S_8
  ➔ Growth of Li_2S

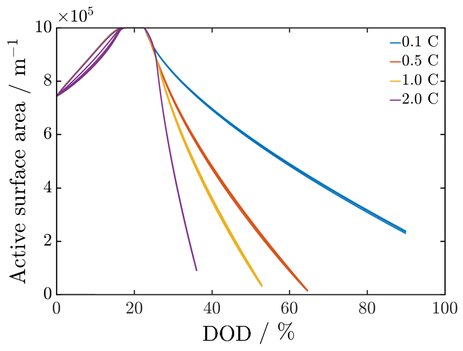
➔ Reverse processes during charge

➔ No degradation: Reversible cycling

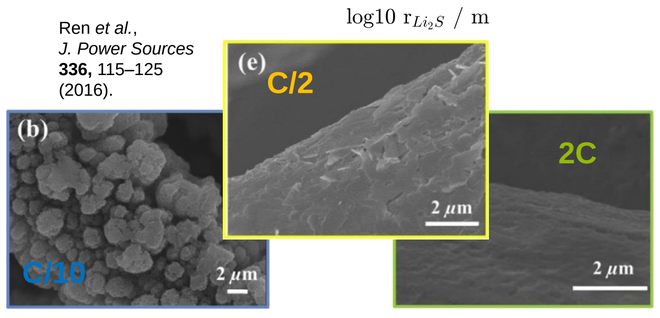
- Cycling data at high C-rates:
  - Loss in capacity & voltage peak during charge
  - Decreasing Li_2S crystal size

➔ Surface passivation

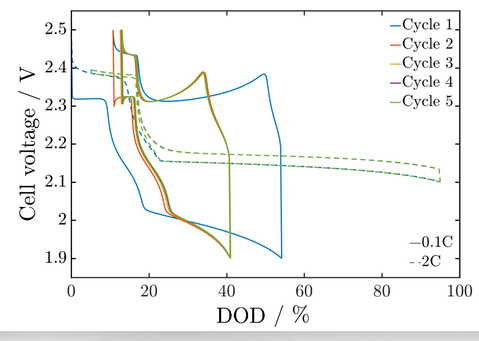




Ren *et al.*, *J. Power Sources* **336,** 115–125 (2016).

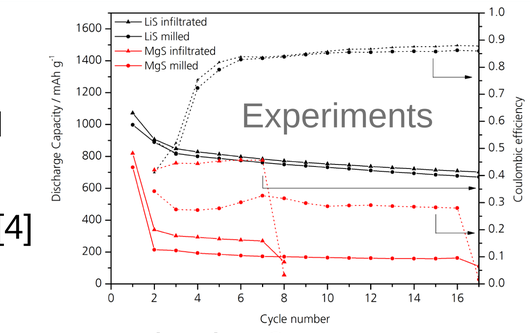


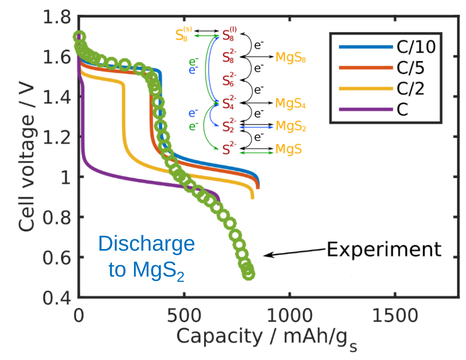
- Constant sulfur loading: 20 vol-%
  ➔ Current collector: large particles
  ➔ Separator: Small particles
  ➔Redistribution of sulfur
- Influence of polysulfide shuttle on sulfur redistribution?



Mg-S cell simulation

- S/C composite cathode preparation
  Milled vs. Melt infiltration
  ➔ Cell model vs. Cell+particle model
- Mg foil anode
- Electrolyte: $Mg(HMDS)_2$ / TEG:DEG [4]





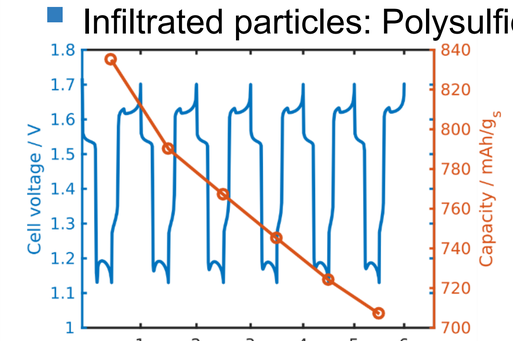
- Discharge mechanism?

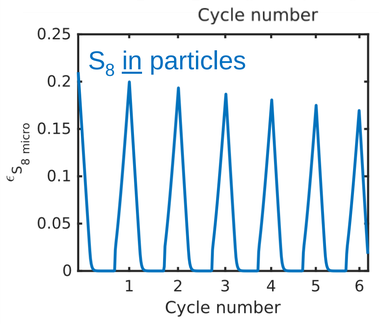
➔ Capacity: Possible end product MgS_2

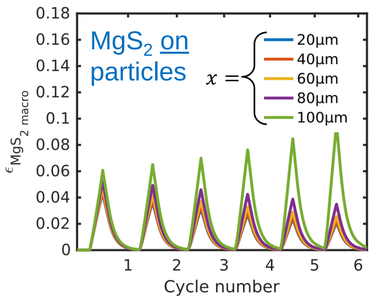
- Sloping potential in 2nd 'plateau'
  - Surface passivation? (→ nucleation)
  - Viscosity effects? (→ no nucleation)

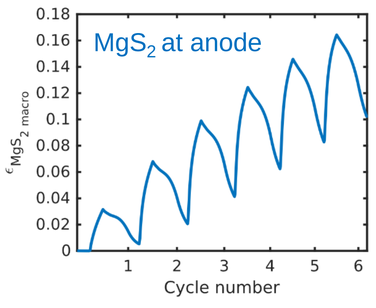
➔ Experimental evidence needed!

- Infiltrated particles: Polysulfide 'bleeding' & shuttle
  - Polysulfides 'escape' from particles
    ➔ S_8 in particles decreases
  - Polysulfide migration towards anode
    ➔ MgS_2 film on particles increases
  - Formation of MgS_2 on anode surface
    ➔ Capacity loss









[1] A. F. Hofmann *et al.*, *J Power Sources* **259,** 300–310 (2014).
[2] T. Danner *et al.*, *Electrochim Acta* **184,** 124–133 (2015).
[3] H. Park *et al.*, *J Phys Chem C* **119,** 4675–4683 (2015).
[4] Z. Zhao-Karger *et al.*, *Adv Energy Mater.* **5,** 1–9 (2015).

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